

Formation of collective excitations in quasi-one dimensional metallic nanostructures: size and density dependance.

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We investigate theoretically the formation of collective excitations in atomic scale quasi-one dimensional metallic nanostructures. The response of the system is calculated within the linear response theory and random phase approximation. For uniform nanostructures a transition from quantum single particle excitations to classical plasmon scaling is observed, depending on the system length and electron density. We find crucial differences in the scaling behavior for quasi-one dimensional and three-dimensional nanostructures. The presence of an additional modulating on-site potential is shown to localize electrons, leading to the response function that is highly sensitive to the number of electrons at low fillings.

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The creation, amplification and control of plasmon excitations in nanostructures (nanoplasmonics) promise an extreme usefulness in near-field scanning microscopy, single molecule detection and other applications [1, 2]. The recent advances in the fabrication and control of low-dimensional nanostructures at atomic resolution (for example, see [3, 4]) make possible control of the interaction of these systems with electromagnetic radiation on a quantum-mechanical level. For example, clusters of Au atoms, arranged in linear chains on a NiAl(100) surface [3], promise to be good candidates for the purpose of local field enhancements, as well as for other applications, including optical media with a negative refractive index, and subwavelength focusing of electromagnetic radiation. Thus, it becomes necessary to examine the fundamental aspects of light-matter interaction of these systems with electromagnetic radiation.

It is known that in small nanostructures one can observe *both* collective modes and single particle excitations (for example, see [5, 6]). Since for many situations strong local field enhancement in nanostructures is due to collective plasmon excitation [7], it becomes a fundamental question: how many electrons is enough to create collective (plasmon) response in a metallic nanostructure, and what is the role of the nanostructure's geometry in the formation of the collective response?

Because of the significant inherent finite-size gaps in such systems, it is essential to perform a detailed quantum-mechanical analysis that identifies the relevant energy scales for the different types of modes. In this paper we study the nature of electronic excitations in quasi-one dimensional metallic nanostructures, investigating the transition between single-particle and collective response as a function of system size, electron density and on-site potential.

In the present approach, the excitation spectrum is determined using linear response theory within the random phase approximation (RPA). We consider how the characteristic excitation energies scale with the system size and electron density.

First, we find that for a fixed number of electrons N_{el} , and variable size L of a quasi-one dimensional system, there is a transition from multiple single-particle excitations to a single dominant collective plasmon-like resonance. The typical size at which the single-particle excitations converge into a single plasmon peak, we denote as the critical size L_{cr} . For relatively small sizes of the system the observed L^{-2} scaling of the single-particle transitions can be qualitatively explained in terms of a quantum particle in a box picture. We denote this regime as "quantum". For larger sizes of the system the plasmon frequency scales as $L^{-1/2}$, that is consistent with the classical plasmon resonance frequency scaling $\omega_p \propto \sqrt{n}$, where $n = N_{el}/L$ is the electron density. We denote this regime as "classical".

Second, we investigate how the critical size L_{cr} depends on the electron density in quasi-one dimensional systems. It is known [6], that for three-dimensional nanostructures the formation of the collective response occurs for smaller system sizes with increasing of the electron density. This is intuitively understandable, since for higher electron densities there are more electrons in the nanostructure which can participate in the collective oscillations. In our simulations we find that for a fixed size L of a quasi-one dimensional system, for lower electronic densities the plasmon resonance is recovered, whereas for higher densities response of the system is found to be consistent with quantum single-particle excitations. This observation is in contrast with the optical response of three-dimensional nanostructures. We give a qualitative explanation of the observed effect based on the different scaling of the Fermi velocity in quasi-one dimensional and three-dimensional quantum systems.

Furthermore, we study formation of collective response in spatially inhomogeneous systems. We suggest that such

systems can be assembled with the same technique [3, 4], but using different species of atoms. A local potential is introduced at alternating atomic sites, and the effect of this modulation on the energy levels is examined. A simple model of consecutive semi-infinite wells is proposed to analyze the excitation spectrum and system response as a function of the electron density. Finally, we investigate the changes in the electromagnetic response for a quantum system which undergoes a transition from extended plane waves to localized wave functions, as the strength of the on-site potential is varied.

Let us consider the response to a time-varying external electromagnetic field with frequency ω in a quasi-one dimensional nanostructured system. We assume an atomic chain of N atoms and length L , that is modeled by a lattice with N sites with the inter-site distance a . We assume the total number of electrons N_{el} in the system, and electrons can freely move along the chain. This assumption seems to be valid since the direct measurement of atomic chains [3] demonstrates that the eigenstates of electrons are in a good agreement with a model of free electrons in an infinite well potential. The Hamiltonian for an electron with a background potential $V(x)$ can be written as $H = -\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial x^2} + V(x)$, where m^* is the effective electron mass. The background potential is either taken to be uniform or varies from site to site. The corresponding eigenproblem is solved by numerical diagonalization.

Within the RPA approximation, the dielectric function is given by [8]:

$$\epsilon^{RPA}(q, \omega) = 1 - V(q)\chi_0(q, \omega), \quad (1)$$

where χ_0 is the retarded density-density correlation function for pair-bubble interactions. For a system with eigenenergies E_i and corresponding Fermi distribution functions, $f_i = 1/(\exp(E_i/k_B T) + 1)$, the density-density correlation function in one dimension is

$$\chi_0(q, \omega) = \frac{1}{L} \sum_{ij} \frac{f_i - f_j}{\hbar(\omega + i\gamma) + E_i - E_j} |M_{ij}|^2, \quad (2)$$

with matrix elements $M_{ij} = \langle i | e^{iqx} | j \rangle$ between eigenstates i and j . γ is a small level broadening constant. The Fourier transform of the Coulomb potential in one dimension is given by $V(q) = 4\pi e^2 \ln(qa)$ [8], where the lattice spacing a is used as a cut-off for the low- q divergence. In the following calculations we focus on the long-wavelength limit $q \rightarrow 0$.

From the dielectric response, the loss function, $\mathcal{L}(q, \omega)$ can be obtained via

$$\mathcal{L}(q, \omega) = \text{Im } \epsilon^{-1}(q, \omega). \quad (3)$$

Collective (plasmon) excitation appears as a large spike in the loss function, which occur when the real part of ϵ vanishes and the imaginary part of ϵ is sufficiently small.

Let us now focus on the dependence of the characteristic resonance frequencies ω_i on the size of the system, specifically looking for a possible transition from quantum to classical scaling. The excitation energies can be determined by the zeros in the dielectric function, and depend on the difference between the eigenenergies of occupied and unoccupied states. Let us give an analysis of the two limiting cases: for small system sizes and large system sizes, correspondingly.

For small system sizes, one can describe the system as a quantum mechanical infinite square well of the length L . The eigenenergies are expected to scale as $E_l = l^2 \pi^2 \hbar^2 / (2m^* a^2 L^2)$, where $l = 1, 2, \dots$ is an integer quantum number, and $t = \frac{\hbar^2}{2m^* a^2}$ is the characteristic energy scale in the system. In the region dominated by the single electron transitions, the multiple poles in $\mathcal{L}(q, \omega)$ are hence expected to scale as L^{-2} in the quantum regime. In contrast, the excitation spectrum for a quasi-one dimensional system in the limit of $L \rightarrow \infty$ and in the long-wave-length limit $q \rightarrow 0$, is known to be dominated by a collective response at the plasma frequency [8]:

$$\omega_p \approx qa\omega_0 |\ln(qa)|^{1/2} + O(q^2), \quad (4)$$

with $\omega_0 = \sqrt{2ne^2/m^*a^2}$, where n is the electron density. Keeping the number of electrons in the system fixed, the electron density scales as $n \propto L^{-1}$, and the plasmon energy is expected to scale as $\omega_p \propto L^{-1/2}$. This scaling behavior is also valid for three-dimensional nanostructures, assuming scaling of only one dimension of a nanostructure, while keeping the other two dimensions fixed.

To summarize, from our analysis, one can predict two different scaling regimes for frequencies of the most pronounced excitations in the system ω_i , with the changes of the system size, while the number of electrons N_{el} is fixed. The first scaling regime is $\omega_i \propto L^{-2}$, in this regime most excitations have single-particle nature. We called this regime "quantum". In the second scaling regime the single particle poles merge into one plasmon resonance ω_p , which scales as $\omega_p \propto L^{-1/2}$. We denote this regime as "classical".

In Fig. 1 the poles of the dielectric response function are plotted as a function of the system size for a fixed number of electrons of $N_{el} = 50$, considering chain lengths with 4 to 64 sites. Each circle represents a peak in the loss function,

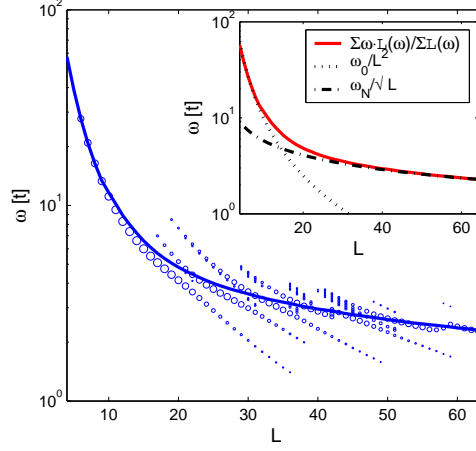


FIG. 1: Low energy poles in $\mathcal{L}(q, \omega)$ as a function of system size, L (in units of the lattice spacing, a), for a fixed number of electrons $N_{el} = 50$. The solid line is a weighted average of $\mathcal{L}(q, \omega)$ in frequency space. $\gamma = 0.05$ t, $q = 0.05$ a^{-1} . In the inset is shown the transition from quantum L^{-2} to classical $L^{-1/2}$ scaling.

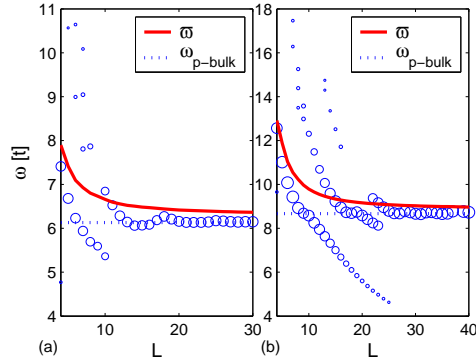


FIG. 2: Low energy poles in $\mathcal{L}(q, \omega)$ for constant electron density, n . The dotted line is the plasmon resonance $L \rightarrow \infty$. $\gamma = 0.05$ t. (a) $n = 1$ electron per site, $\omega_p = 6.1$ t (b) $n = 2$ electrons per site, $\omega_p = 8.7$ t.

with the diameter of the circle proportional to its strength. The solid line is the weighted average over all the poles, given by

$$\bar{\omega} = \frac{\sum_i \omega_i \times \mathcal{L}(q, \omega_i)}{\sum_i \mathcal{L}(q, \omega_i)}. \quad (5)$$

As the length of the chain is increased, the finite-size energy spacings decrease, and the poles eventually merge into a single plasmon feature [6]. In the inset, the weighted loss function is fitted by the quantum ($\propto L^{-2}$) and classical ($\propto L^{-1/2}$) scaling forms. From the figure it is evident that there is a smooth transition from a quantum regime for small atomic chains to a classical regime for longer chains. The intersection of the two fits yields a critical length scale, L_{cr} that depends on the electron density, the effective mass and the atomic spacing. For the parameters chosen for Fig. 1, $L_{cr} \approx 14a$. Additionally, we check that the plasmon resonance given by Eq.(4) is recovered in the limit of long chains.

Now, let us investigate how the critical size L_{cr} depends on the electron density in the system. In Fig. 1 the number of electrons has been kept fixed so that the electron density n and the dominant plasmon frequency ω_p decrease with increasing of the system size. It is difficult to reproduce this situation with differently doped semiconductor nanorods[9], and impossible with real atoms. In order to model realistic atom chains with diffract number of atoms [3] we keep the electron density $n = N_{el}/L$ constant and change the system size L .

In Figs. 2(a) and (b), the loss function poles are plotted as a function of the system size for densities of 1 and 2 electron(s) per site. For a fixed electron density, the single-particle excitation frequencies are expected to scale in the quantum regime (small L) as $\omega_i \propto ((N_{el} + i)^2 - N_{el}^2)L^{-2}/\hbar \propto L^{-1}$, where $N_{el} = nL$, and then approach

a constant value ω_p in the bulk ($L \rightarrow \infty$). The solid line in Fig. 2(a) represents the average frequency given by Eq.(5), and the dotted line represents the plasmon resonance, which occurs at $6.1t$ for a filling of one electron per site. For this case the critical length is determined by the length for which the dominant pole converges to within 1% of its $L \rightarrow \infty$ value. Using this criterion, the critical length is $L_{cr} \approx 17a$ for a filling of 1 electron per site. In Fig. 2(b), the plasmon resonance is $8.3t$, and the critical length is $L_{cr} \approx 24a$ for a filling of 2 electron per site. For size $L = 20a$ illustrated by Fig. 2(b) one has twice electrons in the system than in Fig. 1(a), but surprisingly, there is no established collective response. This example illustrates the crucial difference in response of quasi one dimensional and three-dimensional nanostructures. For quasi-one dimensional systems the critical length L_{cr} increases with the electron density n , whereas it is expected to decrease with density in three dimensions. Below we present our analysis of the anomalous behavior of the critical length L_{cr} .

The characteristic distance for collisionless plasma is the distance when the averaging of the oscillating field for a moving particle happens [10]. For degenerate electron gas it is the distance at which an electron travels at Fermi velocity v_F during one period of the collective field oscillation $L_{cr} \approx 2\pi v_F / \omega_p$. At the same time, the Landau damping, which is closely connected with the spatial dispersion of plasma, occurs also for a critical wave vector $k_{cr} = 2\pi / L_{cr} \approx \omega_p / v_F$. One can alternatively formulate the criterion, that the collective excitations, i.e. plasmons, do not damp for the phase velocities in plasma $v_{ph} = \omega_p / k_{cr}$ much larger than the typical single particle velocity v_F [10]. Since $\omega_p \propto \sqrt{n}$ and the Fermi velocity scales differently with electron density n in one- and three- dimensions, the critical length depends on the density of electrons as $L_{cr} \sim n^{1/2}$ in quasi-one dimensional ($L_{cr} \sim n^{-1/6}$ in three-dimensional cases), consistent with the results found in Figs. 2(a) and (b).

We suggest to check our prediction experimentally by measuring response of atomic chains made of mono- (such as potassium or sodium) and multivalent atoms, for example, aluminium. Based on our analysis, formation of collective (plasmon) response should be observed for *shorter* chains made of *monovalent* atoms and for *longer* chains made of *multivalent* atoms. On the contrary, in the case of three-dimensional nanostructures, like spherical clusters, the formation of plasmon collective mode will be observed for smaller radius of clusters made of multivalent atoms.

Let us now consider inhomogeneous quasi-one dimensional systems made of different species of atoms. Alternatively, one can consider a chain of coupled artificial atoms made of semiconductor quantum dots with controlled number of electrons in the system. Model such systems we assume an on-site potential that takes on alternating values between consecutive atomic sites. Starting with a small system to understand the underlying delocalization effects, the wave functions of the low-energy eigenstates in a double well are plotted in Fig. 3. These illustrate the formation of bonding and anti-bonding combinations, which in the thermodynamic limit of a multi-well chain merge into degenerate energy bands. For clarity, the eigenfunctions in this figure are offset by their energy gap with the ground state, $\epsilon_i - \epsilon_0$. The eigenenergies of lowest four states, i.e. bound states within the well, are doubly degenerate and well separated from the higher states, reminiscent of the spectrum of an atom. As the eigenenergies approach the barrier height, the spacing between energies decreases and a transition occurs from localized to delocalized states, as observed in $\psi_4 - \psi_6$.

For sufficiently large alternating on-site potentials and low electron densities, the dominant low-energy excitations of larger chains can be approximated by consecutive quasi-infinite wells, connected via perturbative tunneling matrix elements, Γ . To illustrate this point, consider first the case of two wells. Using leading-order perturbation theory, the eigenstates of this system are $\epsilon'_{i\pm} = \epsilon_i \pm \Gamma$, where ϵ_i are the eigenenergies of isolated infinite wells. This is a good approximation as long as $\Gamma \ll |\epsilon_i - \epsilon_j|$. Then, for even number of electrons N_{el} , the dominant transitions occur between the energy levels within the individual wells $\approx \epsilon_i$ and ϵ_{i+1} . However, for odd number of electrons N_{el} , transitions are also allowed between bonding and anti-bonding states $\epsilon'_{i\pm}$ and $\epsilon'_{i\mp}$.

In Fig. 3(b) the corresponding poles of the dielectric loss function are shown for increasing number of electrons N_{el} in the system. For odd numbers of electrons at low densities, the lowest excitation corresponds to the transition between ψ_0 and ψ_1 for one electron and between states ψ_2 and ψ_4 for three electrons. In contrast, the higher-energy excitations close to $\omega = 15t$ correspond to transitions between energy bands, and are the lowest available excitation for commensurate fillings. With increasing number of electrons, a single low-energy pole starts to dominate the excitation spectrum. This excitation is a precursor of the collective plasmon mode, and it scales as $\sqrt{N_{el}}$, as indicated by the solid line.

The effects discussed for the two-well case are amplified by increasing the number of wells. For example, the near degeneracy of the low-energy states increases with the number of wells, such that for N identical wells, there will be N states with nearly degenerate energies. For commensurate fillings, the excitation spectrum is then dominated by transitions between the lowest two energy bands. As more electrons are added, intra-band transitions, which occur on a scale of Γ , become more dominant.

In Fig. 4, the poles in the loss function of an 11-site chain are compared for a uniform on-site potential (a) and an alternating potential (b). Each circle represents a peak in the loss function, and the solid lines connect the poles with the maximum loss. In the uniform case, Fig. 4(a), there are several energy bands that increase *linearly* with increasing

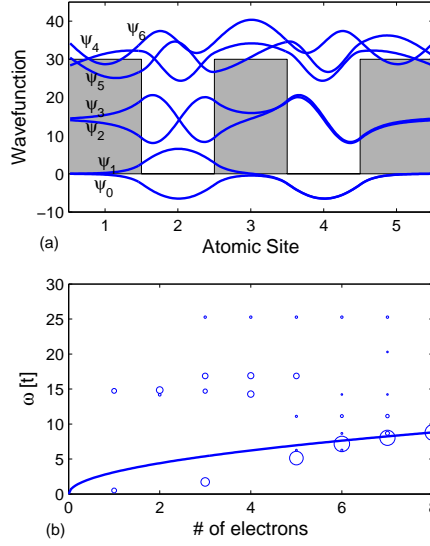


FIG. 3: (a) Electronic wave functions of a double well with on-site potential, $V_{os} = 30 t$, offset by $\epsilon_i - \epsilon_0$. The on-site potential is shown by the shaded region; (b) excitation energies in the dielectric response function for this potential. The size of the circles represents the corresponding oscillator strength.

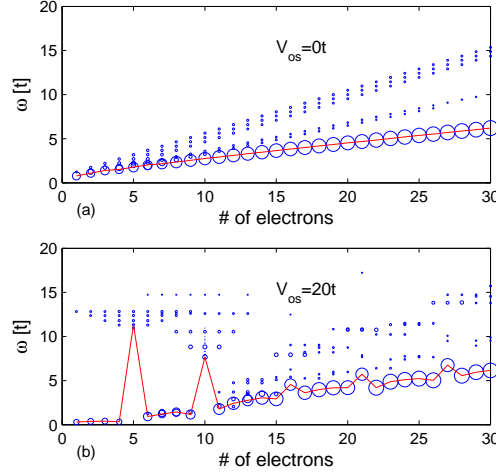


FIG. 4: Poles in the loss function of a chain with $N = 11$ sites, $\gamma = 0.05 t$, $q = 0.05 a^{-1}$. (a) Uniform on-site potential = $0 t$; (b) alternating on-site potential = 0 or $20t$. The thin line connects the loss function peak with maximum intensity.

number of electrons, as the difference in consecutive eigenenergies $E_{i+1} - E_i \propto (i+1)^2 - i^2$ depends linearly on the quantum number i . As more electrons are added and lower states are filled, transitions occur between eigenstates with higher energies.

In Fig. 4(b), the low-energy poles in the dielectric loss function are shown for the case of an alternating on-site potential, leading to 5 wells of depth $20t$. At low numbers of electrons, the peak absorption energy increases dramatically whenever the number of electrons is a *multiple* of the number of wells, making an analog of a "closed shell". For less than five electrons, the loss function is dominated by transitions between lowest energy states associated with each well. Between five and ten electrons, the dominant transitions are between the second energy state associated with each well. For five electrons the lowest set of eigenstates (shell) is occupied and the dominant transition is between the first and second energy of each well. The pattern repeats again for ten electrons, which corresponds to two electrons per well. Above ten electrons, the highest occupied energy level is comparable to the well height so that the electrons are no longer strongly localized in the wells and the excitation energies approach the energies for the case with the uniform potential. This example illustrates the existence of magic numbers in arrays of alternated local potentials which are expected to be most pronounced at the small number of electrons limit.

In conclusion, we have calculated the dielectric response function of quasi-one dimensional nanostructures within the random phase approximation. Using this approach, we have demonstrated that there is a transition from classical to quantum scaling as a function of the system size and electron density. We determine the critical L_{cr} length at which collective response is established. We find that $L_{cr} \propto n^{1/2}$ in quasi-one dimensional nanostructures, opposite to $L_{cr} \propto n^{-1/6}$ for three dimensional nanostructures. We also suggested an experiment to check our theoretical predictions. For inhomogeneous nanostructures, modeled by alternating on-site potentials, electronic bands are formed via tunneling between adjacent potential wells. Depending on the number of electrons, intra- or inter-band transitions dominate the dielectric loss function, leading to a characteristic sequence of magic fillings. Verification of these model predictions by more sophisticated *ab-initio* calculations and by luminescence experiments, e.g. in $(\text{Al}_x\text{Ga}_{1-x})\text{As}$ layered heterostructures, are anticipated.

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